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## ROLE OF CARBON IN PRODUCTION OF TRANSPARENT CORUNDUM CERAMICS USING THE POWDER ALKOXY TECHNOLOGY

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Poor reproducibility of the transparency of corundum ceramics produced by the alkoxy technology is related to the possibility of penetration of oxidized carbon from alkoxy groups into a solid solution with  $\text{Al}_2\text{O}_3$ . Carbon neutralizes the effect of magnesium oxide additive and intensifies diffusion mass transfer, capture of pores by growing crystals, and polymorphous transformation into corundum. Introduction of carbon as soot or naphthalene into previously decarbonized  $\text{Al}_2\text{O}_3$  powder in the course of dry milling, its subsequent heat treatment in air or in moist  $\text{CO}_2$  medium, and sintering of the samples in vacuum supported this assumption.

Transparent corundum ceramics are widely used in the production of high-pressure sodium tubes. At present, full light transmission of the best samples of such ceramics reaches 94%. Powder for corundum ceramics is produced employing chemical methods, since traditional methods cannot ensure the required level of purity, dispersion, and uniform distribution of sintering additives.

The method of aluminum alkoxide hydrolysis is rather promising for production of extra-pure aluminum oxide powder. Alkoxides are produced through the reaction between the respective metals and alcohol. The high purity required in alkoxides is accomplished through distillation. To attain the same high purity employing other methods would be much more expensive. Hydrolysis transforms an alkoxide into a hydroxide, which in heat treatment is converted into an oxide. The alcohol released in hydrolysis of alkoxide can be recovered and used repeatedly, which makes the process virtually free of waste. The resulting alcohol can be used as an extra-pure product.

By varying the terms of various stages of the process, it is possible to control such powder parameters as dispersion and size distribution of particles within a rather wide range. The distribution of required additives can be carried out by a number of methods. At present there is no ceramic powder production based on the alkoxy technology in Russia.

The object of the present study was to clarify the reasons for the poor reproducibility of the alkoxy technology currently being developed and to offer recommendations which would make it possible to produce and stabilize the quality of the powder for transparent ceramics.

It is generally recognized that in order to produce transparent ceramics by standard sintering, one should use extra-pure highly disperse narrow-fraction powders with a particle (aggregate) size not more than 1 – 2  $\mu\text{m}$ . Larger particles, due to their low motive force of sintering, cannot produce a perfectly dense body within the technologically suitable time frame.

The main problem in using highly disperse powders consists in the fact that such small particles tend to aggregate. Numerous researchers have demonstrated that the presence of strong large aggregates in the initial ceramic powder results in decreased density of molded products, impedes the consolidation at the early and later sintering stages, and, finally, prevents one from getting poreless ceramics [1 – 3]. Large and strong aggregates at the early phases of sintering result in the formation of large pores. Such pores are very resistant and hard to remove even at the later phases of sintering [3 – 5].

Another significant problem in the production of powder for transparent ceramics is ensuring high purity of the product. The impurities present in powder can cause the emergence of another phase in the ceramics, which will inevitably decrease light transmission. The impurities forming solid solutions with aluminum oxide are able to accelerate recrystallization in the course of firing, which will intensify capturing of pores into crystals and significantly decrease the light transmission of the ceramics. It is known that the additive which is the most frequently used to delay crystal growth in corundum ceramics sintering is magnesium oxide in an amount not more than 0.2 wt.% (below the solubility point). In addition to magnesium oxide, yttrium and lanthanum oxides are widely used in firing of transparent corundum ceramics (USA patents 4182972, 4214666, 4222978,

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4495116). Some impurities (silicon, iron, and titanium oxides, etc.) are capable of being reduced by sodium vapor in ceramic lamp tubes, which decreases their light transmission and strength.

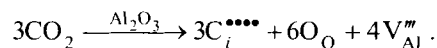
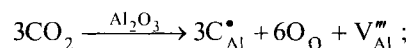
In the present study, additives of magnesium, lanthanum, and yttrium nitrate solutions were added to water used in hydrolysis of aluminum tri-*sec*-butoxide solution in *sec*-butyl alcohol. The poor reproducibility of the ceramic's transparency and conversion of the powder to  $\alpha$ - $\text{Al}_2\text{O}_3$  in heat treatment suggested that a certain significant factor is not appropriately controlled. Petrographic studies demonstrated that small pores in opaque samples are captured by large crystals. The cause of this could be poor distribution of the sintering additive. However, the method used by us provided for introduction of additives at the phase of alkoxide hydrolysis, which was known to ensure significantly better distribution uniformity than the method successfully used in the industry, when these elements are introduced into  $\alpha$ - $\text{Al}_2\text{O}_3$  powder as salts.

An assumption was made that the instability of transparency results and the opaque sites in ceramics can be caused by the presence or absence of carbon that penetrates into corundum ceramics from the alkoxy groups. The possibility of carbon penetration into aluminum oxide was discussed in [6]. However, the powder in that study had a gray color, whereas our powder was white. The penetration of carbon into silicon dioxide was reported in [7], when the latter was produced by heat treatment of the hydrolysis product TEOS. The powder in this case also had a gray color, and the author believes that carbon was present in the powder in the form of fullerenes.

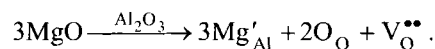
Owing to oxygen volatility, oxygen vacancies arise at crystal boundaries, which provides for a higher diffusion coefficient of oxygen in the polycrystalline sample than that of the metal cation. [8]. With the vacancy mechanism which is typical of most oxides, it is necessary to introduce additives increasing the concentration of cation vacancies in order to accelerate the diffusion mass transfer in ceramics [8]. This is precisely what can happen as carbon incorporates into the aluminum oxide lattice.

Assuming that carbon forms a solid solution with aluminum oxide, this can account for accelerated crystal growth, which leads to capture of pores and loss of transparency of ceramics. Heat treatment of aluminum hydroxide in an oxidizing medium to convert it into oxide ought to ensure the oxidation of carbon. This is indicated as well by the white color of the powder. Another evidence of the presence of oxidized carbon is the fact that an attempt to remove it (from the powder which produced opaque ceramics) through long-term exposure at the maximum heat-treatment temperature in oxidizing conditions did not increase the transparency of the ceramics. Moreover, it was observed that firing in hydrogen produced significantly better transparency than firing in vacuum, since the reduction of carbon facilitates its removal

from the solid solution. As oxidized carbon forms a solid solution, the following defect-forming reactions are possible:

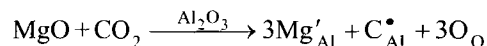


These reactions increase the concentration of aluminum vacancies and, due to the Schottky equilibrium, neutralize the effect of the magnesium oxide additive which causes the formation of oxygen vacancies, according to the reaction



The presence of oxygen vacancies delays the diffusion mass transfer in oxides, which delays crystal growth and polymorphic transformations in ceramics [9 – 11].

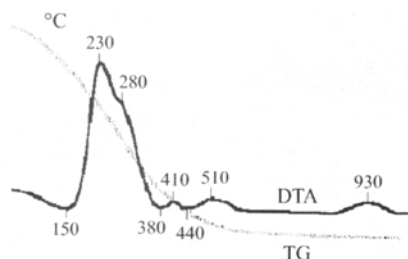
It should be noted, as well, that the presence of oxidized carbon can facilitate the dissolution of magnesium oxide in corundum, since, in accordance with the equation



the presence of magnesium and carbon (IV) oxides in corundum in equimolar quantities does not necessarily result in the formation of vacancies in both sublattices. Thus, the presence of carbon oxide in the solid solution offsets the effect of magnesium oxide. A decrease in the oxygen vacancy concentration results in increased diffusion mass transfer. This contributes to an increased rate of crystal growth and crystal capture of the pores. Due to facilitated dissolution of magnesium in corundum, oxidized carbon can decrease magnesium segregation at intergrain boundaries (IGB) impeding recrystallization.

Magnesium segregation at IGB causes the emergence of a charge on the surface, which is neutralized in the boundary area of the crystal by means of the diffuse layer with an increased concentration of oxygen vacancies and a decreased concentration of aluminum vacancies. Thus, the aluminum vacancies are pushed from the boundary area into the crystal core. A decrease in the aluminum vacancy concentration in the boundary area decreases the rate of migration of the boundary (crystal growth), since this requires coordinated migration of aluminum cations and oxygen anions across the IGB and the presence of the respective vacancies. This decreases the probability of aluminum vacancy arising at the IGB which receives an ion migrating across the IGB, and the probability of breaking-off of the ion located at the crystal boundary, i.e., the mass transfer across the boundary which results in crystal growth.

Carbon in small quantities is hard to identify in solid bodies, since it is contained everywhere and can easily penetrate into analyzed samples. All attempts to prove the presence of carbon by direct methods, such as mass-spectrometry



**Fig. 1.** Aluminum hydroxide thermograms; sample heating rate 5°C/min (weight loss 34%).



**Fig. 2.** DTA curve of powder calcined at temperature of 800°C; sample heating rate 5°C/min (weight loss 34%).

analysis, or electron spectra did not yield unambiguous results. The failure of mass-spectrometry analysis can be accounted by the fact that no adequate measures were taken to prevent the penetration of ambient carbon into samples.

To remove carbon, it was decided to try long-term exposures in calcination of a thin layer of hydroxide powder at the temperature of 800°C, when the powder exists in the form of  $\gamma\text{-Al}_2\text{O}_3$ . The  $\gamma\text{-Al}_2\text{O}_3$  powder (petrographic and x-ray phase analysis data) in vacuum yielded transparent ceramics. The samples exhibited high shrinkage (around 30%). This was accounted for by the volume decrease in conversion of  $\gamma\text{-Al}_2\text{O}_3$  into corundum in firing. Further on, the presence of carbon was identified from transparency of ceramics, and the firing shrinkage value was used to estimate the completeness of  $\gamma\text{-Al}_2\text{O}_3$  conversion into corundum.

As a consequence of carbon removal, the temperature of conversion to corundum was higher than in the powders containing carbon (Fig. 1, the eroded peak at 930°C). Figure 2 shows the DTA curve for the powder from which carbon was removed at 800°C (the polymorphic transition peak is observed at temperature 1155°C).

To prove the effect of carbon, the following experiment was performed. Employing calcination at 800°C,  $\gamma\text{-Al}_2\text{O}_3$  powder was prepared, which produces transparent ceramics and at the same time exhibits high shrinkage, i.e., according

to our assumption, it does not contain carbon. Carbon was deliberately introduced into this powder in the course of joint dry milling with soot or naphthalene (2 wt.%). Dry milling facilitated the penetration of soot or naphthalene into the internal pores of agglomerates [12]. For reference purpose, pure  $\gamma\text{-Al}_2\text{O}_3$  was subjected to similar milling. The resulting powders were heat-treated in air and in a moist  $\text{CO}_2$  medium to convert them into corundum. All powders after heat treatment were white. According to the petrographic and x-ray phase analysis data, the reference sample heat-treated in air contained only around 5%  $\gamma\text{-Al}_2\text{O}_3$ , whereas the samples with soot and naphthalene were completely transformed to corundum. The reference sample and the soot-containing sample heat-treated in moist  $\text{CO}_2$  contained around 25%  $\gamma\text{-Al}_2\text{O}_3$ , whereas the samples with naphthalene were completely transformed to corundum.

The powders were compressed in tablets and fired in vacuum at a temperature of 1800°C. Data on the shrinkage and transparency of the samples (transparency ranking by a 10-grade scale) are shown in Table 1. An increased content of  $\gamma\text{-Al}_2\text{O}_3$  phase in the powder produced a perceptible increase in shrinkage.

As can be seen, introduction of carbon in the form of soot or naphthalene followed by heat treatment in air resulted in decreased transparency and shrinkages, compared to the sample without additives. In our opinion, this supports the hypothesis for the effect of carbon captured from the alkoxy groups on the transparency of corundum ceramics. Heat treatment of  $\gamma\text{-Al}_2\text{O}_3$  without carbon additives in moist  $\text{CO}_2$  medium slightly increased the corundum content, compared to heat treatment in air, which was manifested in shrinkage decrease from 18.3 to 25.8%, but the transparency of the ceramics in this case did not decrease. After heat treatment in moist  $\text{CO}_2$ , the most transparent samples were those with soot and naphthalene additives, and furthermore, naphthalene additive resulted in the complete conversion to corundum, as shown by the low shrinkage after firing and x-ray phase analysis data. Presumably, moist  $\text{CO}_2$  acts as an oxidizer. This medium causes the removal of the greater part of carbon from soot before the beginning of the polymorphous transition; therefore, the shrinkage in this case is the same as in the reference sample without additives. Carbon from naphthalene is preserved up to the moment of polymorphous transition; it ensures complete conversion to corundum and is completely removed during the transition. The higher degree of transparency compared to the reference sample can

**TABLE 1**

Parameter	Air			Moist $\text{CO}_2$		
	Without additive	Carbon-bearing additive		Without additive	Carbon-bearing additive	
		Soot	Naphthalene		Soot	Naphthalene
Shrinkage, %	28.3	16.7	17.5	25.8	25.8	16.7
Transparency	7	4	3	7	9	9

be caused by the modification of the structure of aluminum oxide powder agglomerates, which takes place on removal of carbon.

Dry milling of  $\gamma\text{-Al}_2\text{O}_3$  containing soot presumably results in mechanical capturing of sufficiently large soot fragments into aluminum oxide agglomerates. During subsequent heat treatment in air, part of the carbon does not have time to burn out and remains inside the sealed pores. This leads to the conversion of the powder to corundum, as shown by x-ray phase analysis and petrographic data and the decrease in shrinkage and transparency of the ceramics.

In dry milling of  $\gamma\text{-Al}_2\text{O}_3$  with naphthalene, the latter sublimates and as a vapor phase penetrates into the finest pores. This facilitates its penetration into the sealed pores in the form of significantly smaller inclusions than those of soot. These smaller inclusions with a high degree of probability could oxidize in air and not remain inside the sealed pores up to the moment of the powder conversion to corundum; therefore, the shrinkage in the samples containing naphthalene is somewhat lower than in the samples with soot.

The situation changes when moist  $\text{CO}_2$  is used. Treatment in moist  $\text{CO}_2$  brought about a complete removal of soot before the beginning of the polymorphous transformation. This produced the same level of shrinkage as in the sample without additive. The carbon from naphthalene under these conditions persisted up to the beginning of the polymorphous transition and was removed upon its completion, which provided for low shrinkage and high transparency.

The performed experiments support the view that carbon penetrating into the powder from soot and naphthalene produces the same results with respect to the  $\gamma - \alpha$ -transition and transparency as the residual carbon after decomposition of alkoxy groups. The obtained results suggest the following mechanism of carbon penetration in corundum ceramics during the hydrolysis of alkoxides and its behavior in heat treatment and firing. Carbon penetrates into corundum from alkoxy groups. The evolution of carbon from alkoxy groups can take one of three directions. The greater part of carbon is removed at low temperatures through the oxidation of alkoxy groups, possibly due to a reaction with chemically bonded water. Part of the remaining hydroxides or modifying additive oxides can react with carbon dioxide and form oxycarbonates or carbonates. This oxidized carbon bonded in carbonates is positioned in agglomerates at a relatively small depth. Almost all of it most probably has time to be removed before the start of the polymorphous transition. Its penetration into sealed pores is unlikely. If such were the case, the sample without additives heat-treated in moist  $\text{CO}_2$  would have been converted to corundum to a much greater extent, which did not happen in the experiment.

Carbon that is dangerous to transparency can penetrate into the sealed pores of hydroxide agglomerates from alkoxy groups during hydrolysis, or hydrolyzate aging, drying, or dry milling. A subsequent heat treatment intended to convert

hydroxide to oxide can lead to part of these organic groups inside the deep sealed pores of agglomerate changing into coke. As heat treatment proceeds, the carbon content will increase.

Thus, carbon from alkoxide can penetrate into sealed pores of aluminum oxide. Most probably, this first happens in the form of a carbon cluster, as described in [13]. The conservation or non-conservation of carbon in a sealed pore is determined by the unstable state of the system. This is a typical bifurcation state when a system acquires increased sensitivity to external parameters and to internal fluctuations [14].

A pore with carbon inside can be incompletely sealed (microcracks, dislocations, boundaries). Carbon oxidation with formation of gaseous products through increased pressure ( $2\text{C} + \text{O}_2 = 2\text{CO}$ ) can produce and expand a channel linking an internal pore with the ambient oxidizing medium. This will ensure the open state of the pore and the conditions for complete burning of the carbon. In the case where structural perfection prevails, the pore can become sealed. The pore surface is enriched with additives of magnesium, yttrium, and lanthanum oxides. As oxidation proceeds, the pressure of carbon oxides increases, and pre-nuclei of magnesium, lanthanum, and yttrium carbonates are formed on the surface. If the pressure is high, the carbonates inside a submicron pore will not decompose. It is possible that carbonates or oxycarbonates facilitate the formation of corundum seeds. Part of the carbonates in these conditions can form solid solutions with  $\gamma\text{-Al}_2\text{O}_3$  and accelerate its diffusion transformation into corundum (the last of the above specified reactions). The Headwal effect ought to accelerate the formation of solid solutions and the polymorphous transformation.

Opening or closing of pores containing carbon is a bifurcation. A slight modification of the partial pressure of carbon oxides can be sufficient for changing the direction of the system evolution. In the calcination of hydroxide powder poured in a narrow crucible (diameter 10 mm, height 40 mm), the carbon from the bottom layers of the powder was completely removed, and the ceramic became transparent, whereas in the upper layers it was not removed, and the sample became opaque. The content of water vapor and carbon dioxide in the bottom layers of the powder was higher than in the upper layers, and carbon is much more fully removed in such a medium (Table 1), which was reflected in the transparency. The small size of carbon inclusions formed when naphthalene is used led to a prerequisite for part of the pores in the moist  $\text{CO}_2$  medium to remain sealed, which led to conversion of the powder to corundum and low shrinkage of the ceramic. However, all the carbon had time to be removed in the course of the polymorphous transformation, which provided for high transparency.

Thus, carbon from alkoxy groups can penetrate into sealed pores and then, in an oxidized form (possibly, in the form of magnesium, lanthanum, and yttrium carbonates), can form a solid solution with  $\gamma\text{-Al}_2\text{O}_3$ , which intensifies the diffusion mass transfer, facilitates polymorphous conversion to

corundum and the capture of pores by growing crystals in sintering, and decreases the transparency of the ceramic. The penetration or non-penetration of carbon into a sealed pore is a bifurcation, which makes the process increasingly sensitive to external disturbances and internal fluctuations and leads to poor reproducibility of the results.

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